

FORM-U.S. PATENT & TRADEMARK OFFICE 39 DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE  
(Rev. 10-96)

**TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371**

ATTORNEY'S DOCKET NUMBER

000500-128

U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.5)

Unassigned

PRIORITY DATE CLAIMED

10 January 1996

INTERNATIONAL APPLICATION NO.  
PCT/SE96/01698INTERNATIONAL FILING DATE  
18 December 1996

## TITLE OF INVENTION

A METHOD OF PRODUCING AN ABSORBENT MATERIAL, ~~AN~~ ABSORBENT MATERIAL AND ABSORBENT  
ARTICLES INCLUDING THE MATERIAL IN QUESTION

APPLICANT(S) FOR DO/EO/US

Kent MALMGREN and Bengt WIDBERG

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
  2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
  3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and the PCT Articles 22 and 39(1).
  4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
  5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
    - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
    - b. ☒ has been transmitted by the International Bureau.
    - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
  6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
  7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
    - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
    - b. ☐ have been transmitted by the International Bureau.
    - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
    - d. ☐ have not been made and will not be made.
  8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
  9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
  10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Items 11. to 16. below concern other document(s) or information included:**
11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
  12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
  13. ☒ A FIRST preliminary amendment.  
☐ A SECOND or SUBSEQUENT preliminary amendment.
  14. ☐ A substitute specification.
  15. ☐ A change of power of attorney and/or address letter.
  16. ☒ Other items or information:

INTERNATIONAL SEARCH REPORT; PCT FORM IPEA/416; AND INTERNATIONAL PRELIMINARY EXAMINATION REPORT.

|  |              |  |            |  |    |
|--|--------------|--|------------|--|----|
| U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.50)<br><b>Unassigned</b>   |              | INTERNATIONAL APPLICATION NO.<br><b>PCT/SE96/01696</b> |            | ATTORNEY'S DOCKET NUMBER<br><b>000500-128</b>                        |    |
| 17. <input checked="" type="checkbox"/> The following fees are submitted:  |              |  |            | <b>CALCULATIONS</b>  |    |
| <b>Basic National Fee (37 CFR 1.492(a)(1)-(5)):</b><br>Search Report has been prepared by the EPO or JPO ..... \$930<br>International preliminary examination fee paid to USPTO (37 CFR 1.482) ..... \$720.00<br>No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) ..... \$790.00<br>Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$1070.00<br>International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) ..... \$98.00<br><div style="text-align: right; margin-top: 10px;"><b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b></div>  |              |  |            | <div style="text-align: center; font-size: 1.2em;">\$ 1,070.00</div> |    |
| Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).  |              |  |            | \$   |    |
| Claims   | Number Filed | Number Extra   | Rate       |  |    |
| Total Claims   | 15 -20 =     | 0  | X\$22.00   | \$ 0   |    |
| Independent Claims   | 1 -3 =       | 0  | X\$82.00   | \$ 0   |    |
| Multiple dependent claim(s) (if applicable)  |              |  | + \$270.00 | \$   |    |
| <b>TOTAL OF ABOVE CALCULATIONS =</b>   |              |  |            | \$ 1,070.00  |    |
| Reduction for 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).  |              |  |            | \$   |    |
| <b>SUBTOTAL =</b>  |              |  |            | \$ 1,070.00  |    |
| Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).   |              |  |            | \$   |    |
| <b>TOTAL NATIONAL FEE =</b>  |              |  |            | \$ 1,070.00  |    |
| Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +   |              |  |            | \$ 40.00   |    |
| <b>TOTAL FEES ENCLOSED =</b>   |              |  |            | \$ 1,110.00  |    |
|  |              |  |            | Amount to be: refunded   | \$ |
|  |              |  |            | charged  | \$ |
| <p>a. <input checked="" type="checkbox"/> A check in the amount of \$ <u>1,110.00</u> to cover the above fees is enclosed.</p> <p>b. <input type="checkbox"/> Please charge my Deposit Account No. <u>02-4800</u> in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.</p> <p>c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>02-4800</u>. A duplicate copy of this sheet is enclosed.</p> <p><b>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</b></p> <p>SEND ALL CORRESPONDENCE TO:</p> <div style="display: flex; justify-content: space-between; margin-top: 20px;"> <div style="width: 45%;"> <p>Ronald L. Grudziecki<br/>BURNS, DOANE, SWECKER &amp; MATHIS, L.L.P.<br/>P.O. Box 1404<br/>Alexandria, Virginia 22313-1404</p> </div> <div style="width: 45%; text-align: center;"> <p>SIGNATURE</p> <p><u>William C. Rowland</u></p> <p>NAME</p> <p><u>30,888</u></p> <p>REGISTRATION NUMBER</p> </div> </div> |              |  |            |  |    |

July 8, 1998

12 Rec'd PCT/PTO 08 JUL1998

Patent  
Attorney's Docket No. 000500-128

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

|                             |   |                            |
|-----------------------------|---|----------------------------|
| In re Patent Application of | ) |                            |
|                             | ) |                            |
| Kent MALMGREN et al.        | ) | Group Art Unit: Unassigned |
|                             | ) |                            |
| Application No.: Unassigned | ) | Examiner: Unassigned       |
|                             | ) |                            |
| Filed: July 8, 1998         | ) |                            |
|                             | ) |                            |
| For: A METHOD OF PRODUCING  | ) |                            |
| AN ABSORBENT MATERIAL,      | ) |                            |
| AN ABSORBENT...QUESTION     | ) |                            |

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Prior to examination of the above-identified patent  
application please amend the application as follows:

IN THE CLAIMS:

*The following amendments refer to the claims received in  
the International Application on March 25, 1998.*

Please amend claims 3, 5, 7, 10, 11, 12, 13, and 15 as  
follows:

Claim 3, line 1, delete "or Claim 2".

Claim 5, lines 1 and 2, change "any one of the preceding  
Claims" to --Claim 1--.

Claim 7, lines 1 and 2, change "any one of Claims 1-4" to  
--Claim 1--.

09/101341

Application No. Unassigned  
Attorney's Docket No. 000500-128

Claim 10, lines 1 and 2, change "any one of Claims 7-9" to  
--Claim 7--.

Claim 11, lines 1 and 2, change "any one of the preceding  
Claims" to --Claim 1--.

Claim 12, lines 1 and 2, change "any one of the preceding  
Claims" to --Claim 1--.

Claim 13, line 2, change "any one of the preceding Claims"  
to --Claim 1--.

Claim 15, lines 3 and 4, change "any one of Claims 1-12"  
to --Claim 1--.

**REMARKS**


In the event that there are any questions concerning this  
amendment, or the application in general, the Examiner is

Application No. Unassigned  
Attorney's Docket No. 000500-128

respectfully urged to telephone the undersigned attorney so  
that prosecution of the application may be expedited.

Respectfully submitted,

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By:   
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Date: July 8, 1998

WO 97/25463

1

**A METHOD OF PRODUCING AN ABSORBENT MATERIAL, AN  
ABSORBENT MATERIAL AND ABSORBENT ARTICLES INCLUDING  
THE MATERIAL IN QUESTION**

5 **TECHNICAL FIELD**

The present invention relates to a method of producing polysaccharide fibre, the polysaccharide fibre thus produced and an absorbent article which includes polysaccharide fibres.

10

**BACKGROUND OF THE INVENTION**

Superabsorbents, that is to say absorbent material which is capable of absorbing several times, normally more than ten times, its own weight of water or body fluid, is used in absorbent articles, such as diapers, incontinence guards and sanitary napkins, to enhance the absorbency of the absorbent body of the article and also retention capacity, the remainder of the absorbent body normally consisting of cellulose fibres, so-called fluff pulp.

20 Polyacrylic acid is the polymer most used as superabsorbent non-renewable base. Polyacrylic acid is produced from oil. Since crude oil is a natural resource that is non-renewable, the use of oil as a starting material in the manufacture of polyacrylic acid creates a problem from an environmental aspect.

25 With the intention of resolving this problem, endeavours have been made to produce superabsorbents on the basis of renewable primary materials. These primary materials have included the different polysaccharides, such as starch and cellulose.

WO 97/25463

PCT/SE96/01698

2

One polymer that has been used to a great extent in this context is carboxymethyl cellulose. This is a cellulose derivative with carboxymethyl as a substituent. The properties of the polymer are contingent on the degree of polymerization, DP, and the degree of substitution, DS. Carboxymethyl cellulose is relatively cheap and has high affinity to water-based liquids.

However, the admixture of carboxymethyl cellulose in absorbent articles such as diapers, incontinence guards and sanitary napkins is associated with serious drawbacks. When the article is wetted during use, the carboxymethyl cellulose will dissolve and therewith increase the viscosity of the liquid discharged by the wearer. This dramatically reduces the liquid dispersion rate. So-called gel blocking occurs. Carboxymethyl cellulose that has a degree of substitution below 0.35 is not soluble in water and could therefore be used favourably in absorbent articles with regard to the aspect of gel blocking. However, carboxymethyl cellulose that has a degree of substitution below 0.35 has poor absorption properties in comparison with polyacrylates. In other words, the carboxymethyl cellulose must have a degree of substitution greater than 0.35 in order to have good absorption properties, although such carboxymethyl cellulose is soluble in water and therewith presents a gel blocking problem.

Another drawback with the superabsorbents that are commercially available at present is the administration form. The superabsorbent is normally added to the article in which it shall be included in the form of grains, flakes or granules. A special metering apparatus is required to add superabsorbent in this form, and it is difficult to obtain uniform distribution of superabsorbent in the fibrous pulp body.

Superabsorbent in fibre form would be easier to meter. Because the absorbent body into which the superabsorbent is to be administered normally consists of fibres, there is a danger of superabsorbent particles separating-out from the fibre matrix. This

WO 97/25463

PCT/SE96/01698

3

problem is alleviated with superabsorbents in fibre form. Although polyacrylate fibres are commercially available, they have not been used to any great extent. This is probably due to their high price and poor swellability.

- 5 A number of attempts have been made to produce polysaccharide fibres for use in sanitary products. WO 93/12275 discloses solvent spinning of polysaccharide fibre. However, the swelling properties of polysaccharide fibres produced in accordance with known techniques is too poor for such fibres to be of interest as a substitute for conventional superabsorbent material.

10

## OBJECT OF THE INVENTION

- An object of the present invention is to provide a superabsorbent material which is based on renewable primary material and which has an acceptable performance capacity in comparison with conventional superabsorbent materials.

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Another object of the invention is to produce a superabsorbent material in an administration form which facilitates uniform metering of the superabsorbent material to a pulp body.

20

## SUMMARY OF THE INVENTION

- A method for producing a polysaccharide fibre of the kind mentioned in the introduction and having properties which enable the aforesaid problems associated with conventional superabsorbent material to be avoided is characterized in accordance with the invention by dissolving the polysaccharide in a solvent, extruding the solution down into a bath which includes a water-miscible organic solvent, preferably an alcohol, such as methanol, ethanol or isopropanol, or a ketone, such as acetone, and a cross-linking agent, such as a polyelectrolyte or a metal salt,

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19 March 1998

4

PCT/SE96/01698

preferably a salt of a divalent, trivalent or quadrivalent ion, such as calcium, magnesium, iron, aluminium or zirconium.

## DESCRIPTION OF THE INVENTION

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Those polysaccharides that can be used to produce a polysaccharide fibre in accordance with the invention are, for instance, carboxymethyl cellulose, starch, cellulose xanthane, gelan, chitin, chitosan, guar gum, alginate.

10

As before mentioned, carboxymethyl cellulose, which is a cellulose derivative, is particularly well-suited for this purpose. The properties of the polymer are contingent on the degree of polymerization, DP, and the degree of substitution, DS.

15

The degree of polymerization, DP, denotes the number of monomer units in the polymer chain that influence the viscosity of an aqueous solution of the polymer.

20

The degree of substitution, DS, denotes the mean number of carboxymethyl substituents in the polymer chain. The degree of substitution influences the swelling properties of the polymer, and a degree of substitution above 0.35 gives a water-soluble polymer.

25

As before mentioned, a degree of substitution above 0.35 is desirable in order to obtain a high absorbency. However, this would result in a water-soluble polymer and therewith create gel-blocking problems.

Consequently, it would be desirable to produce a polysaccharide, for example, a carboxymethyl cellulose, that had a degree of substitution greater than 0.35 and which did not dissolve in water. This object is realized in accordance with the invention, by cross-linking the polymer. This cross-linking may be covalent or ionic.

WO 97/25463

PCT/SE96/01698

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The use of conventional cross-linkers to cross-link the polymer, such as epichlorhydrin and formaldehyde, would cause the coagulate to precipitate very slowly and fasten to the extrusion nozzle, therewith creating serious disturbances in a large-scale process.

According to the invention, the polymer is ionically cross-linked with the aid of polyelectrolytes or polyvalent metal ions, especially calcium, zirconium, aluminium or iron(III). When carboxymethyl cellulose is to be cross-linked, it is probable that cross-linking is effected by the formation of bonds between the carboxyl groups. Cross-linkers in the form of salts give fibres that are easily spun. The salt in which the polyvalent metal ion or the polyelectrolyte is present shall be soluble in water. The counter-ion to the metal ion or the polyelectrolyte, in other words the anion, is selected accordingly. Chloride is a suitable anion in this respect.

15

The cross-linked superabsorbent is then distributed in an absorbent body, which is normally comprised of cellulose pulp. The pulp may be in reels, bales or sheets which are dry-defibrated and converted into a fluffed state to form a pulp mat. As before mentioned, the material in the absorbent body may be cellulose fibres.

Examples of other fibres conceivable in this regard are cotton fibres and synthetic fibres. It is also known to use foamed material in the absorbent body.

20

The problem of administering a superabsorbent in grain, flake or granule form evenly in the absorbent body is solved in accordance with the invention by choosing another administering form, namely a fibre form.

25

These fibres are produced in accordance with the invention by solvent spinning. Solvent spinning is carried out by pumping a polymer solution to a spinning nozzle, and extruding the solution into a bath containing a water-miscible organic solvent,

WO 97/25463

PCT/SE96/01698

6

such as an alcohol. This solvent causes the polymer to precipitate in the form of fibres.

5 The extrusion bath may also contain water. The volume of water in the extrusion bath is determined by the fact that a given lowest organic solvent content is required to obtain good quality fibres. The lowest organic solvent content is about 70 vol%. The extrusion bath may thus contain about 0-30 vol% water.

10 As the polysaccharide which was earlier dissolved in water precipitates in the extrusion bath, the bath will become enriched with water. For the above-said reason, this water must be removed continuously to prevent the organic solvent content falling beneath about 70 vol%. The extrusion bath also includes one or more cross-linking agents in addition to the organic solvent. This method results in the simultaneous forming of fibres and cross-linking of the polymer.

15 The fibres are reeled-up from the extrusion bath, and dried and cut into appropriate lengths. An appropriate fibre length is 2-20 mm, preferably 4-8 mm. After this has been done, the fibres can be admixed in absorbent bodies intended for use in absorbent articles, such as diapers, incontinence guards and sanitary napkins.

20 According to one alternative embodiment of the invention, the fibres may also be subjected to post-treatment, in which the fibres are cross-linked covalently. Surprisingly, this covalent cross-linking of the fibres has been found to greatly increase the capillary liquid-retaining capacity of the fibres.

25 The following explanation as to why the covalent cross-linking enhances the liquid-retaining capacity of the fibres shall be seen solely as an hypothesis of how the invention can be assumed to function. The described hypothesis, or theory, shall not be considered as limiting the scope of the invention, but shall be seen solely as a

WO 97/25463

PCT/SE96/01698

7

conceivable model of the manner in which the invention works, with the intention of facilitating an understanding of the invention.

The reason why the covalently bonded fibres have a surprisingly good retention ability may be because the covalently cross-linked fibres swell rapidly and copiously. The risk of gel-blocking decreases; a fibre network containing the covalently cross-linked fibres has very large pores in a swollen state. The fibres expand quickly and copiously, particularly longitudinally, which favours the expansion on the network in which the covalently cross-linked fibres are mixed and thereby enhances dispersion of liquid, or fluid, in the network.

This covalent surface cross-linking of the fibres can be achieved with various conventional cross-linkers, for example: 2,4,6-trichloro-1,3,5-triazine, epichlorohydrin, bis(epoxypropyl) ether, dichloroethane, divinylsulfone, ethylene glycol-bis(epoxypropyl) ether, formaldehyde, vinyl cyclohexane dioxide, 1,3-dichloro-2-propanol, 1,3-bis( $\beta$ -hydroxy-t.-chloropropoxy)-2-propanol, 1,3-bis( $\beta$ -hydroxy-t.-chloropropoxy) ethane, 1,2:3,4-diepoxybutane, 1,1:5,6-diepoxyhexane, 2,3-dibromo-1-propanol, 2,3-dichloro-1-propanol, 2,2-dichloroethyl ether, methyl bis(acrylamide), N,N'-dimethylol(methylbis(acrylamide)), trisacrylol hexahydro-triazin, acrylamidemethyl chloroacetamide, 2,4,6-trichloropyrimidine, 2,4,5,6-tetrachloropyrimidine, cyanuric chloride, triallyl cyanurate, dichloroacetic acid, phosphorus oxychloride, bis(acrylamido) acetic acid.

These cross-linkers and cross-linking methods using these cross-linkers are described by Dean, Ferguson and Holst in the book "Absorbency", edited by P.K. Chatterjee, Elsevier Science Publishing Company, 1985.

In accordance with the invention, polysaccharide fibres may be produced by moulding (casting) as an alternative to extrusion. The polysaccharide fibres are

WO 97/25463

PCT/SE96/01698

8

sprayed into a bath which contains solvent and one or more cross-linkers as described above, both when extruding and casting the fibres. However, when casting the fibres the solution is not sprayed through a nozzle as in the case with extrusion, but is instead sprayed onto a plate rotating in the bath.

5

The polysaccharide fibres produced in accordance with the invention can now be used as conventional superabsorbents, in other words can be mixed with fluff pulp or applied in layers between fluff pulp or between tissue layers. They can also be combined with other superabsorbents.

10

It will be understood that the invention is not restricted to the combinations described here, but that all combinations of solvents, cross-linkers and polysaccharides are included in the inventive concept.

## 15 Embodiments

### Example 1 - Spinning of CMC-fibres having different aluminium contents

#### Equipment

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Rayon spinning laboratory equipment was used, this equipment being shown in Figure 1.

The equipment comprised:

25 A pressure chamber, shown in detail in Figure 2.

A gear pump.

A spinning nozzle.

A rectangular plexiglass tank measuring 890x195x190 mm, to be used as an extrusion bath.

WO 97/25463

PCT/SE96/01698

9

A beaker 10 containing a de-aerated carboxymethyl cellulose (CMC) solution 1 was placed in a pressure chamber 2. A lead weight 11 was placed on top of the solution. The chamber 2 was sealed and air having a pressure of 7.5 bars forced the CMC-solution through a steel pipe 12 and via a gear pump 4 to the spinning nozzle 3. The lead weight 11 prevented air from entering between the CMC-solution 1 and the steel pipe 12. The spinning nozzle 3 contained 20 holes 5, each having a diameter of 200  $\mu\text{m}$ .

10 The CMC-solution 1 was extruded out into the extrusion bath 7 through the spinning nozzle 3. The extrusion bath 7 contained ethanol and aluminium chloride.

CMC-fibres 8 were drawn through the extrusion bath with the aid of a variable speed roller 9 driven by an electric motor. The CMC-fibres were held beneath the surface of the extrusion bath with the aid of a glass rod.

The fibres were then washed in ethanol (95%), being held for two minutes in the alcohol. This procedure was repeated two times. The washed fibres were dried at room temperature and then cut into lengths of 6 mm.

20

#### A method of preparing the carboxymethyl cellulose solution

Different concentrations of CMC were tested: 8% Cekol 10000 and 7% Cekol 50000 from Metsä-Särlä Oy. Cekol 10000 and Cekol 50000 had mutually the same DS (0.6-0.9) but Cekol 50000 had a higher DP than Cekol 10000.

25

CMC in granule or powder form was mixed with water. The mixture was stirred (agitated) manually and the mixture then allowed to stand in a closed container for at least two calendar days.

WO 97/25463

PCT/SE96/01698

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The mixture was centrifuged and evacuated alternately, until all air bubbles in the mixture had disappeared. 600 g of the CMC-solution were placed in a plastic beaker (800 ml), the beaker being subjected to a vacuum for thirty minutes in order to  
5 remove air bubbles from the solution.

#### The extrusion bath

The extrusion bath had a volume of 8 l. Originally, it consisted of 95 vol% ethanol  
10 and 5 vol% water. Aluminium chloride was then added to the bath. The amount of aluminium chloride in the bath varied as shown in Figures 3 and 4. The concentration of aluminium chloride fell during the process, as the fibres absorbed the salt. It was therefore necessary to add aluminium chloride during the spinning process. The concentration of aluminium chloride was never allowed to fall by more  
15 than 10% during the process.

#### The aluminium content of the fibres

CMC-fibres were produced with different aluminium contents, by varying the  
20 aluminium content of the extrusion bath. Figure 3 shows the result obtained when using Cekol 10000 as the starting material, while Figure 4 shows the result obtained when using Cekol 50000 as the starting material.

#### Example 2 - Producing CMC-fibres with different baths

25

With the intention of discovering whether or not fibres could be formed in extrusion baths of mutually different compositions, tests were carried out with aluminium salts, iron salts, zirconium salts and magnesium salts in a bath with different solvents. The

WO 97/25463

PCT/SE96/01698

11

CMC used was Cekol 50000. The solvents tested were ethanol, methanol, isopropanol and acetone. The following bath compositions were tested:

| <u>Metal salt</u>  | <u>Liquid salt</u>                    |
|--|---------------------------------------|
| 5  |                                       |
| 1. 4.4 g $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /litre solution   | 95 vol-% ethanol + 5 vol-% water      |
| 2. 4.4 g $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /litre solution   | 95 vol-% methanol + 5 vol-% water     |
| 3. 4.4 g $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /litre solution   | 85 vol-% acetone + 15 vol-% water     |
| 4. 4.4 g $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /litre solution   | 95 vol-% isopropanol + 5 vol-% water  |
| 10   |                                       |
| 5. 5.3 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /litre solution   | 95 vol-% ethanol + 5 vol-% water      |
| 6. 5.3 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /litre solution   | 95 vol-% methanol + 5 vol-% water     |
| 7. 5.3 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /litre solution   | 95 vol-% acetone + 5 vol-% water      |
| 8. 5.3 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /litre solution   | 95 vol-% acetone + 5 vol-% water      |
| 15   |                                       |
| 9. 6.0 g $\text{ZrCl}_4$ /liter solution                             | 95 vol-% ethanol + 5 vol-% water      |
| 10. 6.0 g $\text{ZrCl}_4$ /liter solution                            | 95 vol-% methanol + 5 vol-% water     |
| 11. 6.0 g $\text{ZrCl}_4$ /liter solution                            | 95 vol-% isopropanol + 5 vol-% water  |
| 20   |                                       |
| 12. 15.5 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ /liter solution | 95 vol-% ethanol + 5 vol-% water      |
| 13. 15.5 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ /liter solution | 95 vol-% methanol + 5 vol-% water     |
| 14. 15.5 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ /liter solution | 78 vol-% acetone + 22 vol-% water     |
| 15. 15.5 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ /liter solution | 90 vol-% isopropanol + 10 vol-% water |

## 25 Results

Fibres were obtained with all extrusion bath compositions.



WO 97/25463

PCT/SE96/01698

12

Example 3 - Polyelectrolytes as cross-linkers

CMC-fibres were produced from Cekol 50000 in accordance with the invention,  
5 there being used a spinning bath containing polyelectrolytes dissolved in 80 vol%  
ethanol and 20 vol% water. The compositions of the different spinning baths are  
described below.

|    | <u>Polyelectrolyte</u>    | <u>Trade name</u>   | <u>Content (weight %)</u> |
|----|---------------------------|---------------------|---------------------------|
| 10 | Polyvinyl amine           | Basocoll (BASF)     | 0.05                      |
|    | Polybrene                 | Polybrene (Aldrich) | 0.1                       |
| 15 | (quatarnary<br>polyamine) |                     |                           |

Result

Fibres could be produced in both baths.

[illegible]

19 March 1998

13

PCT/SE96/01698

#### Example 4 - Producing fibres from different types of polysaccharides

Concentrated aqueous solutions were produced from the following polysaccharides.

| 5  | <u>Polysaccharide</u> | <u>Trade name (manufacturer)</u>                | <u>Concentration</u><br><u>(weight %)</u> |
|----|-----------------------|---|---|
|    | CMC                   | Cekol 2000 (Metsä-Serla OY)                     | 12  |
|    | CMC                   | Cekol 4000 (Metsä-Serla OY)                     | 10  |
| 10 | CMC                   | Cekol 10000 (Metsä-Serla OY)                    | 8   |
|    | CMC                   | Cekol 30000 (Metsä-Serla OY)                    | 7.5                                       |
|    | CMC                   | Cekol 50000 (Metsä-Serla OY)                    | 7   |
|    | Guar gum              | Meypro® Guar (Meyhall)                          | 10  |
|    | Bean gum              | Meypro® LBG (Meyhall)                           | 10  |
| 15 | Pectin                | Genu® pectin type X-0905<br>(Copenhagen Pectin) | 5   |

The solutions were then used to produce fibres in accordance with the invention, in a spinning bath consisting of 8 g  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /l in 95 vol% ethanol and 5 vol% water.

## Result

Fibres could be produced from all of these polysaccharides.

25 **Example 5 - Covalent cross-bonding of spun CMC-fibres**

CMC-fibres produced from Cekol 50000 in accordance with Example 1 by spinning in a bath containing 3 g  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /l in 95 vol% ethanol and 5 vol% water were used in this test. 5 g of fibres cut to a length of 6 mm were placed in a glass beaker

WO 97/25463

PCT/SE96/01698

14

containing 250 ml of distilled water and allowed to swell for about one minute. 250 ml of a 2 percent by weight solution of 2,4,6-trichloro-1,3,5-triazin in acetone were then added to the beaker.

- 5 After stirring the bath gently for five minutes, a 2.5 M NaOH-solution was added drop-wise while continuing to stir the bath. A total of 30 ml NaOH-solution were added over a period of fifteen minutes. The bath was then stirred gently for a further thirty minutes, whereafter the liquid was removed and the fibres were washed repeatedly with 95 vol% ethanol. The fibres were then dried at room temperature.

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Example 6 - Characterization of absorption properties with the aid of liquid porosymmetry

Liquid porosymmetry

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A fibre network made of fibres produced in accordance with the invention was characterized with the aid of a PVD-apparatus (Pore Volume Distribution) manufactured by Textile Research Institute, Princeton, U.S.A. The function of the PVD-apparatus is described concisely in Miller, B. and Tyomkin, L., Text. Res. J. 56 (1986) 35 and described briefly below, referring to Fig. 9.

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Liquid was applied to the sample (in this case 0.9% NaCl-solution and so-called synthetic urine, respectively) in an excess amount and the sample allowed to absorb the liquid over a given period (in this case 5 h). The sample 13 was then placed in a chamber 14 on a membrane 15, and a porous plate 16, a mechanical load (in this case 2.5 kPa) in the form of a lead weight being placed on top. The chamber was then sealed-off and the chamber air pressure increased progressively in stages with the aid of a computer-controlled pressurizing system, the liquid being exited from the

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WO 97/25463

PCT/SE96/01698

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sample through a small-pore membrane (in this case a pore size of 0.22 µm). The weight of the liquid pressed from the sample was recorded by a balance scale 17.

5 According to Laplace equation [1], a given pressure corresponds to a given pore radius.

$$\Delta P = \frac{2\gamma \cos\theta}{r} \quad [1]$$

10 where

$\Delta P$  = The pressure necessary for pressing-out liquid hydraulically.

$\gamma$  = The surface tension of the liquid.

$\theta$  = Contact angle between liquid and examined material.

$r$  = Pore radius.

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When surface tension and contact angle are constant, the pressure increase is thus reciprocally proportional to the pore radius.

20 This gives a relationship between pressure difference and liquid volume, which can be described schematically in accordance with the Figure 7 diagram.

When this cumulative relationship is derivated, there is obtained a pore volume distribution as shown diagrammatically in Figure 8. The distribution function reveals the amount of liquid retained by pores of a given size.

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In this work, liquid contained in pores greater than 3 mm has been defined as capillary liquid, and liquid in pores smaller than 3 mm as gel liquid. The capillary

WO 97/25463

PCT/SE96/01698

16

liquid is found in pores between the fibres, whereas the gel liquid is found in the interior of the fibres and in pores on the surfaces thereof.

According to the Laplace equation [1], the pressure required to remove the gel liquid is greater than the pressure required to remove the capillary-bound liquid. It can be said therefore that the gel liquid is "firmly" bound to the material, whereas the capillary liquid is bound less firmly.

A comparison between so-called superabsorbents and pulp fibres shows that the difference in gel-liquid content is very great when the liquid is comprised of water, 0.9% NaCl-solution, so-called synthetic urine or some other substance that swells superabsorbents.

The liquid porosymmetry method thus provides good possibilities of examining the ability of the material to retain firmly-bound liquid, and a distribution function which describes how the capillary, less firmly-bound, liquid is retained in the material.

Figure 9 is a schematic illustration of the construction of the PVD-apparatus.

Fibres from Example 1, spun in a bath containing 3 g  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /l 95 vol% ethanol and 5 vol% water, and fibres from Example 5 were characterized with the aid of the PVD-apparatus described above. Sample bodies were formed from the aforesaid fibres. So-called synthetic urine was used as test liquid and the materials were loaded with a pressure of 2.5 kPa during the measuring process.

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The following materials were also tested for comparison purposes:

08/07/98

19 March 1998

17

PCT/SE96/01698

1. CTMP (Mölnlycke)
2. Sulphate pulp (Korsnäs)
3. Superabsorbent powder, Sanwet® IM 2200D (Hoechst)

5

Result

Table 1 shows the values obtained with regard to gel liquid, capillary bound liquid and the total amount of liquid absorbed.

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Table 1

| <u>Sample</u>    | <u>Gel liquid</u><br><u>g/g</u> | <u>Capillary liquid</u><br><u>g/g</u> | <u>Total liquid</u><br><u>g/g</u> |
|------------------|---------------------------------|---------------------------------------|-----------------------------------|
| CTMP             | 1.37                            | 8.78                                  | 10.75                             |
| Sulphate pulp    | 0.86                            | 6.24                                  | 7.10                              |
| Sanwet® IM 2200D |                                 | 16.85                                 | 16.12      32.97                  |
| CMC-fibres       | 19.90                           | 10.00                                 | 29.90                             |
| Example 1        |                                 |                                       |                                   |
| CMC-fibres       | 14.40                           | 16.85                                 | 31.25                             |
| Example 5        |                                 |                                       |                                   |

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AMENDED SHEET

19 March 1998

18

PCT/SE96/01698

The ability of Sanwet® IM 200D and CMC-fibres to absorb gel liquid was found to be several times greater than the ability of the pulp fibres. A comparison between the CMC-fibres from Example 1 and Example 5 shows that the covalently cross-linked fibres from Example 5 have a greater ability to take-up capillary-bound liquid.

Figures 10 and 11 illustrate the pore volume distribution of the materials tested. It will be seen from Figure 11 that the fibre network comprised of covalently cross-linked CMC-fibres has larger pores than the fibres which are not covalently cross-linked. This should be advantageous from the aspect of flow resistance when liquid shall be transported between the fibres in an absorbent article. The pore structure of the commercial polyacrylate superabsorbent Sanwet® IM 2200D is equivalent to the pore structure of the covalently cross-linked CMC-fibre from Example 5.

#### Example 7 - The swelling capacity of the fibres

Free swelling capacity is defined as the swelling capacity of a material that is not subjected to pressure.

Figure 5 illustrates the free swelling capacity of CMC-fibres produced in accordance with Example 1 from Cekol 50000 and having an aluminium content of 7.7 g/kg. The liquids tested were 0.9% NaCl, synthetic urine and synthetic menstruation fluid. By synthetic urine and synthetic menstruation fluid is meant synthetically prepared liquids which were similar to their natural counterparts with regard to physical properties and chemical composition.

19 March 1998

19

PCT/SE96/01698

Figure 6 illustrates a comparison with regard to free-swelling between CMC-fibres produced in accordance with Example 1 from Cekol 50000 and having an aluminium content of 7.7 g/kg, and two commercially available CMC-materials,

- 5 Aqualon® ACU D-3273 (Hercules) and E228-95 (Hoechst). It will be seen from the Figure that CMC-fibres produced in accordance with Example 1 have a higher free-swelling capacity than the commercially available CMC-materials.



19 March 1998

20

PCT) SE96/01698

**NEW CLAIMS**

1. A method of producing polysaccharide fibres, characterized by dissolving a polysaccharide in a solvent, and spraying the solution into a bath which contains a water-miscible organic solvent and a cross-linker.
2. A method of producing polysaccharide fibres in accordance with Claim 1, characterized by stretching, rolling-up, drying and cutting the polysaccharide fibres after the bath.
3. A method of producing polysaccharide fibres according to Claim 1 or Claim 2, characterized in that the organic solvent is an alcohol or a ketone.
4. A method of producing polysaccharide fibres according to Claim 3, characterized in that the organic solvent is methanol, ethanol, isopropanol or acetone.
5. A method of producing polysaccharide fibres in accordance with any one of the preceding Claims, characterized in that the cross-linker is a polyelectrolyte.
6. A method of producing polysaccharide fibres according to Claim 5, characterized in that the cross-linker is polyvinylamine or Polybrene® (hexadimethrinbromide).
7. A method of producing polysaccharide fibres according to any one of Claims 1-4, characterized in that the cross-linker is a salt where the cation in the salt is a metal ion.

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100 101 102 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198 199 200 201 202 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 280 281 282 283 284 285 286 287 288 289 290 291 292 293 294 295 296 297 298 299 300 301 302 303 304 305 306 307 308 309 310 311 312 313 314 315 316 317 318 319 320 321 322 323 324 325 326 327 328 329 330 331 332 333 334 335 336 337 338 339 340 341 342 343 344 345 346 347 348 349 350 351 352 353 354 355 356 357 358 359 360 361 362 363 364 365 366 367 368 369 370 371 372 373 374 375 376 377 378 379 380 381 382 383 384 385 386 387 388 389 390 391 392 393 394 395 396 397 398 399 400 401 402 403 404 405 406 407 408 409 410 411 412 413 414 415 416 417 418 419 420 421 422 423 424 425 426 427 428 429 430 431 432 433 434 435 436 437 438 439 440 441 442 443 444 445 446 447 448 449 450 451 452 453 454 455 456 457 458 459 460 461 462 463 464 465 466 467 468 469 470 471 472 473 474 475 476 477 478 479 480 481 482 483 484 485 486 487 488 489 490 491 492 493 494 495 496 497 498 499 500 501 502 503 504 505 506 507 508 509 510 511 512 513 514 515 516 517 518 519 520 521 522 523 524 525 526 527 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2622 2623 2624 2625 2626 2627 2628 2629 2630 2631 2632 2633 2634 2635 2636 2637 2638 2639 2640 2641 2642 2643 2644 2645 2646 2647 2648 2649 2650 2651 2652 2653 2654 2655 2656 2657

19 March 1998

21 a

PCT/SE96/01698

15. An absorbent structure in an absorbent article, such as a diaper, an incontinence guard or a sanitary napkin, characterized in that the absorbent structure includes polysaccharide fibres having been produced in accordance with any one of Claims 1-12.

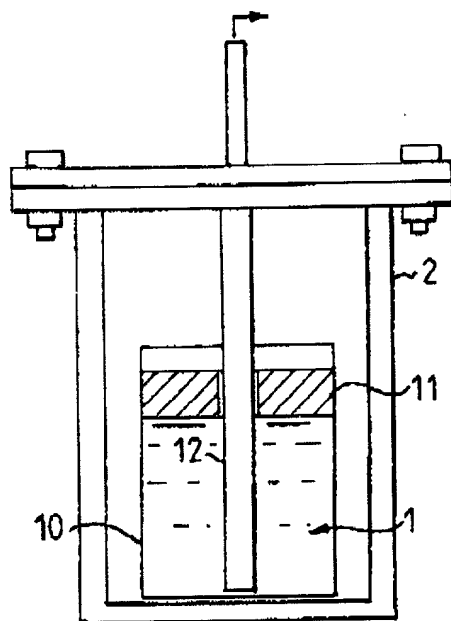
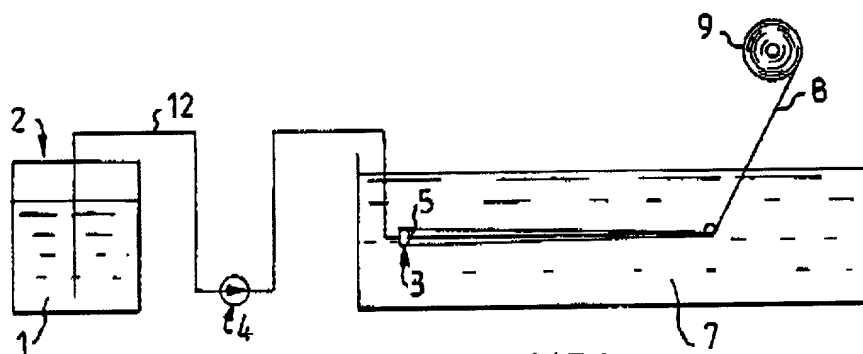
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09/101341

WO 97/25463

PCT/SE96/01698

1/5



SUBSTITUTE SHEET (RULE 26)

09/101341

WO 97/25463

PCT/SE96/01698

2/5

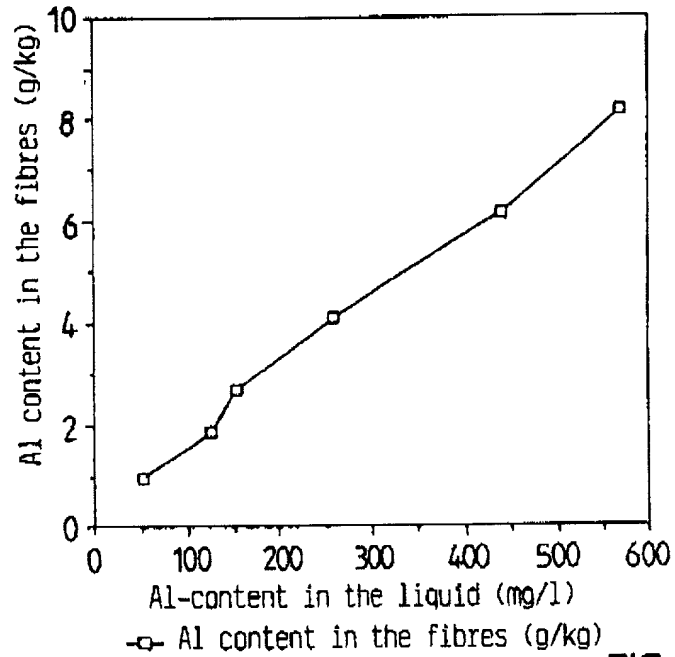
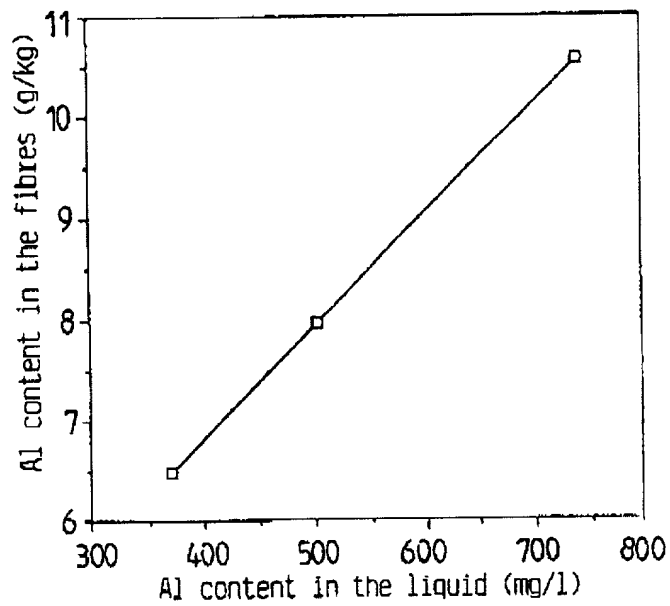


FIG. 3



-□- Al content in the fibres (g/kg)

FIG. 4

09/101341

WO 97/25463

PCT/SE96/01698

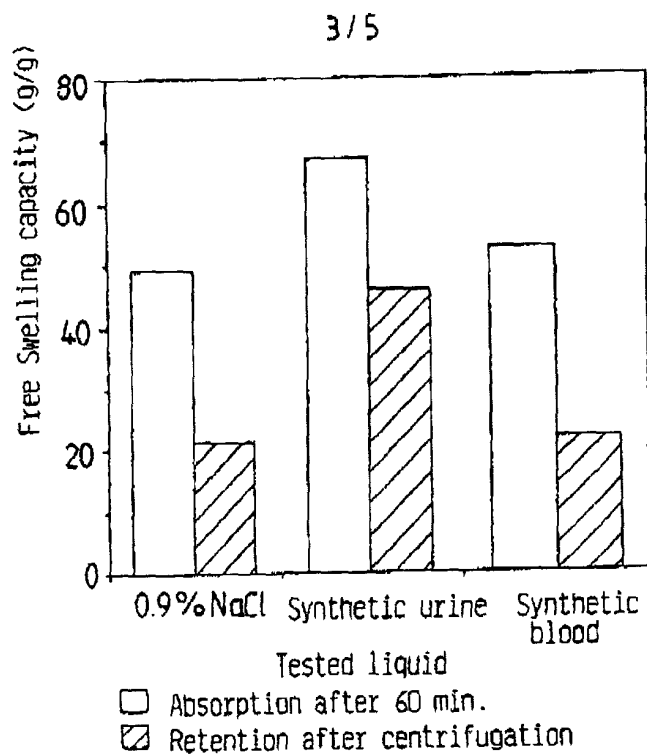


FIG. 5

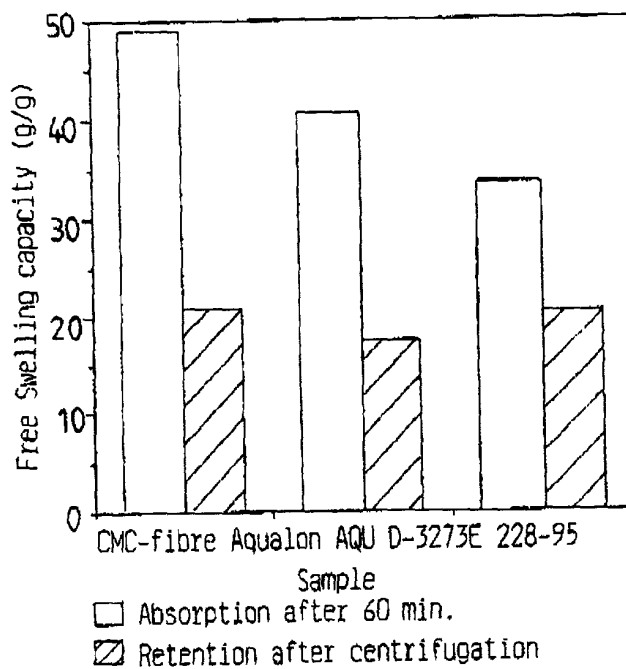


FIG. 6

09/101341

WO 97/25463

PCT/SE96/01698

4/5

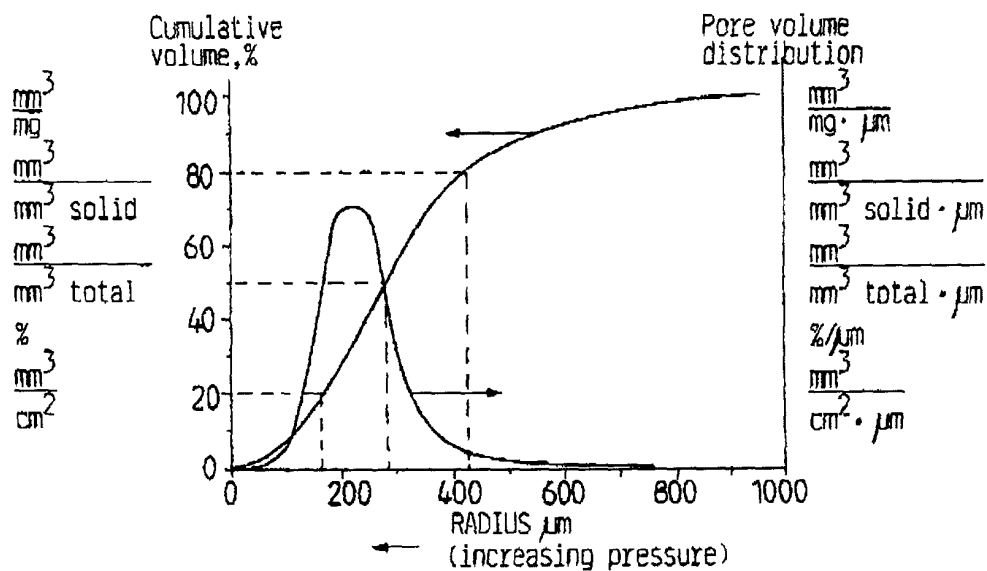
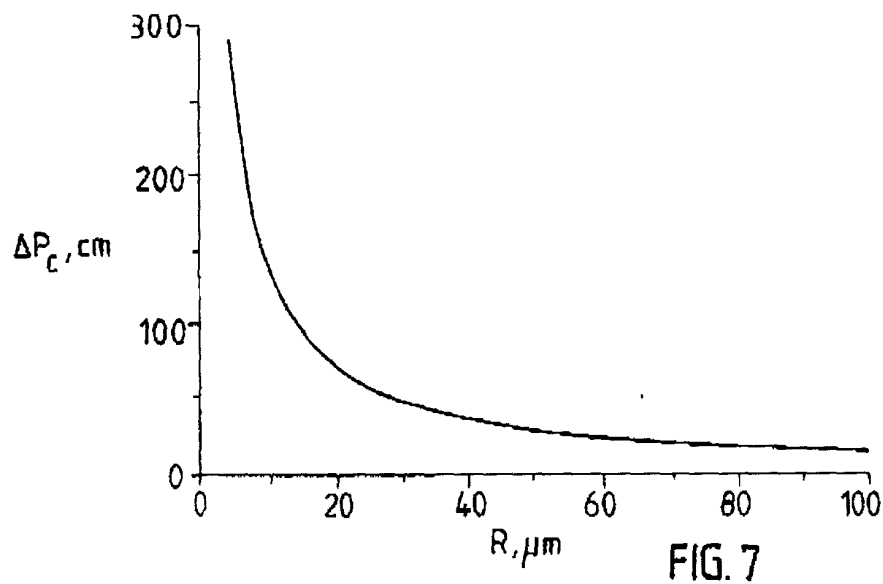


FIG. 8

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WO 97/25463

PCT/SE96/01698

5/5

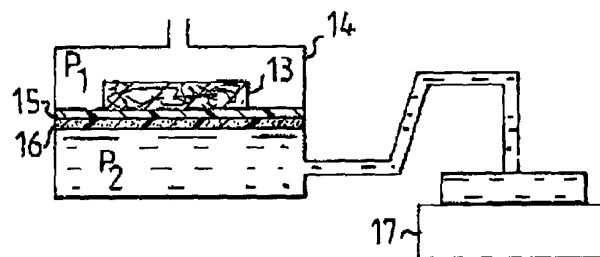


FIG.9

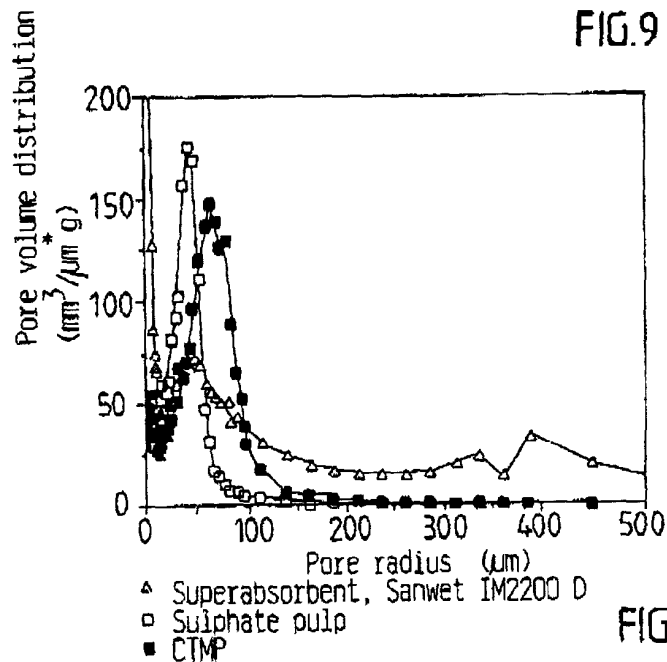


FIG.10

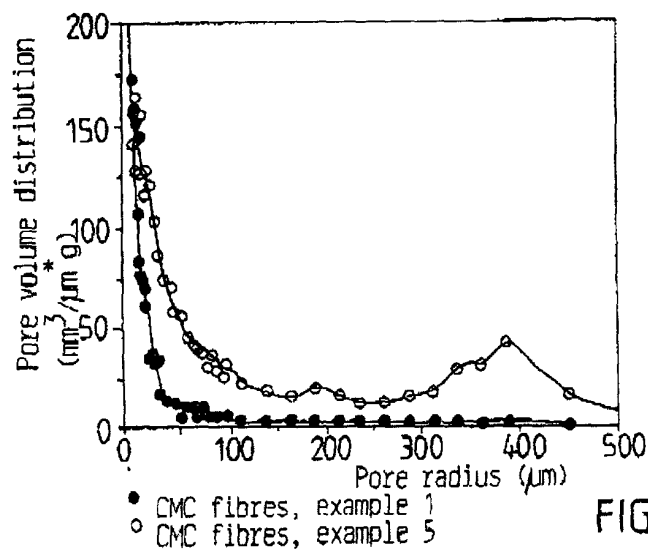


FIG.11



|  |                     |
|--|---------------------|
| <b>COMBINED DECLARATION AND POWER OF ATTORNEY<br/>FOR UTILITY PATENT APPLICATION</b>   | Attorney Docket No. |
| <p>As a below named inventor, I hereby declare that:<br/>         My residence, post office address and citizenship are as stated below next to my name;<br/>         I BELIEVE I AM THE ORIGINAL, FIRST AND SOLE INVENTOR (if only one name is listed below) OR<br/>         AN ORIGINAL, FIRST AND JOINT INVENTOR (if more than one name is listed below) OF THE SUBJECT<br/>         MATTER WHICH IS CLAIMED AND FOR WHICH A PATENT IS SOUGHT ON THE INVENTION<br/>         ENTITLED: <u>A method of producing an absorbent material, an</u><br/> <u>absorbent material and absorbent articles including the material</u><br/>         the specification of which: <u>in question.</u></p> <p>(check <input type="checkbox"/> is attached hereto;<br/>         one) <input checked="" type="checkbox"/> was filed on <u>18 December 1996</u> as</p> <p>Application Serial No. <u>PCT/SE96/01698</u></p> <p>and was amended on _____<br/>         (if applicable)</p> <p>I HAVE REVIEWED AND UNDERSTAND THE CONTENTS OF THE ABOVE-IDENTIFIED SPECIFICA-<br/>         TION, INCLUDING THE CLAIMS, AS AMENDED BY ANY AMENDMENT REFERRED TO ABOVE;</p> <p>I ACKNOWLEDGE THE DUTY TO DISCLOSE INFORMATION WHICH IS MATERIAL TO THE EXAMI-<br/>         NATION OF THIS APPLICATION IN ACCORDANCE WITH TITLE 37, CODE OF FEDERAL REGULA-<br/>         TIONS, Sec. 1.56 (a) which states: "A duty of candor and good faith toward the Patent and Trademark Office<br/>         rests on the inventor, on each attorney or agent who prepares or prosecutes the application and on every other<br/>         individual who is associated with the inventor, with the assignee or with anyone to whom there is an obligation<br/>         to assign the application. All such individuals have a duty to disclose to the Office information they are aware<br/>         of which is material to the examination of the application. Such information is material where there is a substantial<br/>         likelihood that a reasonable examiner would consider it important in deciding whether to allow the application<br/>         to issue as a patent. The duty is commensurate with the degree of involvement in the preparation or prosecution<br/>         of the application.";</p> <p>I do not know and do not believe the said invention was ever known or used in the United States of America<br/>         before my or our invention thereof, or patented or described in any printed publication in any country before<br/>         my or our invention thereof or more than one year prior to said application; that said invention was not in public<br/>         use or on sale in the United States of America more than one year prior to said application; that said invention<br/>         has not been patented or made the subject of an inventor's certificate issued before the date of said application<br/>         in any country foreign to the United States of America on any application filed by me or my legal representatives<br/>         or assigns more than twelve months prior to said application;</p> <p>I hereby claim foreign priority benefits under Title 35, United States Code Sec. 119 and/or Sec. 365 of any<br/>         foreign application(s) for patent or inventor's certificate as indicated below and have also identified below any<br/>         foreign application for patent or inventor's certificate on this invention having a filing date before that of the<br/>         application(s) on which priority is claimed:</p> |                     |

|  |                    |                                      |   |
|--|--------------------|--------------------------------------|---|
| <b>COMBINED DECLARATION AND POWER OF ATTORNEY</b>  |                    | Attorney Docket No.                  |   |
| COUNTRY/INTERNATIONAL  | APPLICATION NUMBER | DATE OF FILING<br>(day, month, year) | PRIORITY CLAIMED  |
| Sweden   | 9600087-2          | 10.01.96                             | YES <input checked="" type="checkbox"/> NO <input type="checkbox"/> |
|  |                    |                                      | YES <input type="checkbox"/> NO <input type="checkbox"/>            |
| I hereby appoint the following attorneys and agent(s) to prosecute said application and to transact all business in the Patent and Trademark Office connected therewith and to file, prosecute and to transact all business in connection with international applications directed to said invention:  |                    |                                      |   |
| <div style="display: flex; flex-wrap: wrap;"> <div style="width: 50%;">           20 William L. Mathis 17,337<br/>           Peter H. Smolke 15,913<br/>           Robert S. Swecker 19,885<br/>           Platen N. Mandros 22,124<br/>           Benson S. Duffell, Jr. 22,030<br/>           Joseph R. Magnone 24,229<br/>           Joel M. Freed 25,101         </div> <div style="width: 50%;">           Norman H. Supno 22,716<br/>           Ronald L. Grudowski 24,970<br/>           Frederick G. Michaud, Jr. 25,003<br/>           Alan E. Kopsicki 25,813<br/>           Regis E. Sluiter 26,999<br/>           Samuel C. Miller, III 27,160<br/>           Ralph L. Freeland, Jr. 18,110         </div> <div style="width: 50%;">           Robert C. Mukai 28,531<br/>           George A. Novak, Jr. 28,223<br/>           James A. LaBarte 28,632<br/>           E. Joseph Gess 28,510<br/>           David D. Reynolds 28,273<br/>           R. Barry Huntington 27,801         </div> </div> |                    |                                      |   |
| and: _____   |                    |                                      |   |
| Address all correspondence to:<br><u>Burns, Doane, Swecker &amp; Mathis</u><br><u>George Mason Building</u><br><u>Washington and Prince Streets</u><br><u>P. O. Box 1404</u><br><u>Alexandria, Virginia 22313-1404</u>   |                    |                                      |   |
| Address all telephone calls to: _____ at (703) 836-6620.   |                    |                                      |   |
| I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.  |                    |                                      |   |
| FULL NAME OF SOLE OR FIRST INVENTOR<br><u>Kent Malmgren</u>  |                    | SIGNATURE<br><u>Kent Malmgren</u>    | DATE<br><u>980604</u>   |
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| POST OFFICE ADDRESS<br><u>Harmonigatan 11C, S-854 63 Sundsvall, Sweden</u>   |                    |                                      |   |
| FULL NAME OF SECOND JOINT INVENTOR, IF ANY<br><u>Bengt Widberg</u>   |                    | SIGNATURE<br><u>Bengt Widberg</u>    | DATE<br><u>980604</u>   |
| RESIDENCE<br><u>Sundsvall, Sweden</u> SEX <u>SEX</u>   |                    | CITIZENSHIP<br><u>Swedish</u>        |   |
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| FULL NAME OF THIRD JOINT INVENTOR, IF ANY  |                    | SIGNATURE                            | DATE  |
| RESIDENCE  |                    | CITIZENSHIP                          |   |
| POST OFFICE ADDRESS  |                    |                                      |   |

☐ Please see attached continuation page for additional inventors.